METHYLENE BLUE ADSORPTION ONTO CROSSLINKED SAGO STARCH

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Special Dedication of This Grateful Feeling to My Beloved father and mother;

Mr. MUHMEDB. ALI and Mrs. HABSAH BT. AB. KADIR

Loving siblings;

NOR NAZIFAH, SALIHAH KAMILAH,

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For Their Love, Support and Best Wishes.

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ABSTRACT

Crosslinked sago starch was prepared by crosslinking native sago starch with sodium trimetaphosphate (CSS-STMP) and epichlorohydrin (CSS-EPCH) as renewable adsorbents. CSS-STMP and CCS-EPCH were used to remove methylene blue (MB) from aqueous solution based on its characterization tests. The adsorption capacity of CSS-STMP and CSS-EPCH were evaluated as a function of pH, adsorbent dosage, initial MB concentration, contact time and temperature. It was favorable for adsorption under condition of pH 7 and at 50 ppm for both adsorbent. The adsorption capacity trend was reduced with increasing adsorbent dosage where 0.05 g dose of adsorbent was chosen. Equilibrium adsorption capacity (q_e) of MB adsorption onto CSS-STMP and CSS-EPCH were 2.224 mg g^{-1} and 1.303 mg g^{-1}, respectively. CSS-STMP adsorbent was employed for further experiment due to its better performance than CSS-EPCH. The equilibrium isotherms were conducted using Langmuir, Freundlich and Tempkin models. It has been demonstrated that a better agreement was Langmuir isotherm with a correlation coefficient (R^2) of 0.990, complete monolayer adsorption capacity (q_m) of 3.731 mg g^{-1}, chi-square test (χ^2) of 0.029% and corresponding contact time of 4 hours. The pseudo-first-order, pseudo-second-order and intra-particle diffusion were used to fit adsorption data in the kinetic studies. The results show that the adsorption kinetic was more accurately described by the pseudo-second-order model with the mechanism via film diffusion where R^2 is 0.999 and variance is 0.152%. The adsorption of MB on CSS-STMP was exothermic and non-spontaneous in nature at temperature of 303K. Regeneration study also indicated that CSS-STMP adsorbent have the potential to be reused at the same adsorption performance for numbers of cycle. The obtained results suggest that CSS-STMP could be a promising candidate as an adsorbent for MB removal.

ABSTRAK

Kanji sagu ikatan-silang disediakan dengan mengikat silang kanji sagu dengan natrium trimetafosfat (CSS-STMP) dan epiklorohidrin (CSS-EPCH) sebagai penjerap yang boleh diperbaharui. CSS-STMP dan CSS-EPCH digunakan untuk menyingkirkan metilena biru (MB) daripada larutan akueus berdasarkan ujian pencirian. Kapasiti penjerapan oleh CSS-STMP dan CSS-EPCH dinilai berdasarkan pH, dos penjerap, kepekatan awal MB, hubungan masa dan suhu. Proses penjerapan adalah lebih tinggi pada pH 7 dan kepekatan awal MB sebanyak 50 ppm untuk kedua-dua penjerap. Trend kapasiti penjerapan berkurangan apabila dos penjerap bertambah di mana dos penjerap 0.05 g telah dipilih. Kapasiti penjerapan (q_e) oleh CSS-STMP dan CSS-EPCH masing-masing adalah sebanyak 2.224 mg g^{-1} dan 1.303 mg g^{-1}. Penjerap CSS-STMP digunakan untuk uji kaji seterusnya disebabkan prestasi yang lebih baik berbanding CSS-EPCH. Oleh itu, penjerap CSS-STMP digunakan untuk eksperimen seterusnya. Keseimbangan isoterma dijalankan menggunakan model Langmuir, Freundlich dan Tempkin. Isoterma Langmuir menunjukkan prestasi baik dengan nilai korelasi pekali (R^2) 0.990, satu lapisan lengkap kapasiti penjerapan (q_m) 3.371 mg g^{-1}, ujian khi kuasa dua (χ^2) 0.029% yang sepadan dengan masa sentuhan 4 jam. Pseudo peringkat-pertama, pseudo peringkat-kedua dan penyebaran intra zarah digunakan untuk menyesuaikan data penjerapan di dalam kajian kinetik. Keputusan menunjukkan penjerapan kinetik adalah lebih tepat diterangkan oleh model pseudo peringkat-kedua dengan mekanisme melalui filem penyebaran di mana nilai korelasi pekali ialah 0.999 dan nilai varians ialah 0.152%. Penjerapan MB oleh CSS-STMP adalah luah haba dan bukan spontan pada suhu 303K. Kajian pertumbuhan semula menunjukkan CSS-STMP mampu untuk digunakan semula pada prestasi penjerapan yang sama. Keputusan yang diperoleh mencadangkan bahawa CSS-STMP boleh dijadikan penjerap alternatif yang baik untuk penyingkiran MB.

TABLE OF CONTENTS

CHAPTER	TITLE		PAGE
	DECLARATION		**ii**
	DEDICATION		**iii**
	ACKNOWLEDGEMENT		**iv**
	ABSTRACT		**v**
	ABSTRAK		**vi**
	TABLE OF CONTENTS		**vii**
	LIST OF TABLES		**xi**
	LIST OF FIGURES		**xii**
	LIST OF SYMBOLS		**xiv**
	LIST OF ABBREVIATIONS		**xvi**
1	**INTRODUCTION**		**1**
	1.1	Research Background	1
	1.2	Problem Statement	4
	1.3	Research Objectives	5
	1.4	Scopes of Research	5
	1.5	Significant of Study	7
	1.6	Thesis Outline	9
	1.7	Summary	10
2	**LITERATURE REVIEW**		**11**
	2.1	Dyes	11
		2.1.1 Classification of Dyes	13

		2.1.1.1 Cationic and Anionic Dyes	14
		2.1.1.2 Methylene Blue	15
		2.1.2 Toxicity Effect of Dyes	17
	2.2	Present Treatment Methods for Dye Removal	18
	2.3	Adsorption	21
		2.3.1 Adsorption Parameters	22
		2.3.2 Application on Adsorption Isotherm Model	30
		2.3.3 Dye Adsorption Kinetic Study	34
		2.3.4 Thermodynamic Study	37
	2.4	Regeneration and Desorption Study	38
	2.5	Adsorbent	39
	2.6	Introduction of Starch	43
		2.6.1 Gelatinization and Retrogradation of Starch	46
		2.6.2 Starch Modification	47
		2.6.2.1 Chemical Modification of Starch	48
		2.6.2.2 Crosslinking Method	49
	2.7	Sago Starch	53
3	**METHODOLOGY**		**56**
	3.1	Introduction	56
	3.2	Materials and Chemicals	57
	3.3	Equipment and Apparatus	57
	3.4	Experimental Procedure	58
		3.4.1 Preparation of Crosslinked Sago Starch Adsorbent	60
		3.4.2 Characterization Procedures of Adsorbent	60
		3.4.2.1 Scanning Electron Microscopy (SEM)	61
		3.4.2.2 Fourier Transform Infrared Spectroscopy (FTIR)	61

		3.4.2.3 X-Ray Diffraction (XRD)	61
		3.4.2.4 Thermo Gravimetric Analysis (TGA)	62
		3.4.2.5 Differential Scanning Calorimeter (DSC)	62
	3.4.3	Concentration Measurement Calibration	63
	3.4.4	Batch Adsorption Experiment	64
		3.4.4.1 Specific Experimental Conditions	65
		3.4.4.2 Uptake Calculation	66
	3.4.5	Desorption	67
	3.5	Summary	68
4		**RESULTS AND DISCUSSIONS**	**69**
	4.1	Introduction	69
	4.2	Characterizations of Adsorbent	70
	4.2.1	Surface Morphology Analysis	70
	4.2.2	Functional Group Analysis	72
	4.2.3	X-Ray Diffraction Pattern Analysis	74
	4.2.4	Thermogravimetric Analysis	76
	4.2.5	Differential Scanning Calorimeter Analysis	77
	4.3	Parameters Effect on MB Removal	79
	4.3.1	Effect of pH	80
	4.3.2	Effect of Adsorbent Dosage	83
	4.3.3	Effect of Initial MB Concentration	85
	4.3.4	Effect of Adsorption Time	87
	4.3.5	Effect of Temperature	89
	4.4	Adsorption Equilibrium Isotherm	90
	4.5	Adsorption Kinetic Studies	95
	4.6	Adsorption Thermodynamics	101
	4.7	Regeneration and MB Recovery	103

5	**CONCLUSIONS AND RECOMMENDATIONS**		**106**
	5.1	Summary of Research Findings	106
	5.2	Suggestions for further research	108
REFERENCES			**110**
Appendix			124

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Physicochemical properties of Methylene Blue	16
2.2	Advantages and limitations of some technologies used for dye removal	19
2.3	Methylene blue removal using various kinds of adsorbents; condition parameters and its adsorption capacity	23
2.4	Adsorption isotherm models, the corresponding linear form, parameters and descriptions	31
2.5	Kinetic models, the corresponding linear form, parameters and descriptions	35
2.6	Advantages and limitations of different adsorbents used in adsorption process for removing dyes	41
2.7	Adsorption capacity for the removal of dyes by starch-based material adsorbents	45
2.8	Comparison on different types of chemical modifications	50
2.9	Chemical composition of Sago Starch	54
4.1	Gelatinization parameters of native sago starch, CSS-STMP and CSS-EPCH	78
4.2	Adsorption isotherm parameters for the MB adsorption onto CSS-STMP	93
4.3	Parameters of pseudo-first-order and pseudo-second-order at different adsorbent dosage and initial MB concentration	98
4.4	Parameters of intra particle diffusion model at different adsorbent dosage and initial MB concentration	100
4.5	Thermodynamic parameters for the adsorption of MB onto CSS-STMP	102

LIST OF FIGURES

FIGURE NO.	TITLES	PAGE
2.1	Dye pollution	12
2.2	Methylene blue solution	16
2.3	Adsorption process on (a) monolayer (b) multilayer	34
2.4	Molecular structure of starch (a) amylose (b) amylopectin	44
2.5	Crosslinking reaction with (a) phosphorus oxychloride, (b) Sodium trimetaphosphate and (c) epichlorohydrin	52
2.6	(a) Sago palm tree (b) sago powder	54
3.1	Research methodology outline	59
3.2	Calibration curves for methylene blue	64
4.1	Scanning electron micrograph of (a) sago starch (b) CSS-STMP (C) CSS-EPCH	71
4.2	FTIR spectrum of native sago starch and crosslinked sago starch with EPCH and STMP	73
4.3	X-ray diffractograms of (a) native sago starch (b) CSS-STMP (c) CSS-EPCH	75
4.4	TGA thermograms of native sago starch and crosslinked sago starch (CSS-STMP and CSS-EPCH)	76
4.5	DSC thermograms of of native sago starch and crosslinked sago starch (CSS-STMP and CSS-EPCH)	78
4.6	Effect of initial pH on the adsorption capacity, q_e of MB Onto CSS-STMP and CSS-EPCH (conditions: adsorbent dosage, 0.5g; initial concentration, C_o, 20 ppm; adsorption time, 240 min and adsorption temperature, 303 K)	82
4.7	Effect of initial pH on the removal efficiency (%) of MB Onto CSS-STMP and CSS-EPCH (conditions: adsorbent dosage, 0.5g; initial concentration, C_o, 20 ppm; adsorption time, 240 min and adsorption temperature, 303 K)	82

4.8	Effect of adsorbent dosage on the adsorption capacity, q_e and removal efficiency, % of MB onto CSS-STMP and CSS-EPCH (conditions: pH, 7; initial concentration C_o, 20 ppm; adsorption time, 240 min and adsorption temperature, 303 K)	84
4.9	Effect of initial concentration on the adsorption capacity, q_e of MB onto CSS-STMP at pH 7 and 0.05 g and pH 7, 0.02 g (conditions: adsorption time, 240 min and adsorption temperature, 303 K)	86
4.10	Effect of adsorption time on the adsorption capacity, q_e of MB onto CSS-STMP at 0.05 g, 50 ppm and 0.05 g, 20 ppm (condition: pH, 7 and adsorption temperature, 303 K)	88
4.11	Effect of adsorption temperature on the adsorption capacity, q_e of MB onto CSS-STMP (condition: pH, 7; adsorbent dosage, 0.05 g; initial MB concentration, 50 ppm; and adsorption time, 240 min)	90
4.12	Plots of fitting of the experimental data with a) Langmuir b) Freundlich and c) Tempkin based on linearization form	92
4.13	Separation Factor for the adsorption of MB onto CSS-STMP	93
4.14	Pseudo-first-order kinetic plots for the adsorption of MB onto CSS-STMP (pH: 7; temperature: 303 K)	97
4.15	Pseudo-second-order kinetic plots for the adsorption of MB onto CSS-STMP (pH: 7; temperature: 303 K)	97
4.16	Intraparticle diffusion kinetic plots for the adsorption of MB onto CSS-STMP (pH: 7; temperature: 303 K)	100
4.17	Van’t Hoff plot for MB adsorption onto CSS-STMP (condition: pH, 7; adsorbent dosage, 0.05 g; initial MB concentration, 50 ppm; and adsorption time, 240 min)	102
4.18	MB adsorption onto CSS-STMP as a function of adsorption cycles. (Adsorption condition: time: 4 h; pH 7, temperature 303K: initial concentration 50ppm. Desorption condition: temperature 303K; dosage: 1mg/ml NaOH; solvent concentration (40:60) water-ethanol mixture; time: 4 h)	105

LIST OF SYMBOLS

$\Delta G°$	-	Gibbs free energy change
$\Delta H°$	-	Enthalpy change of adsorption
ΔHg	-	Enthalpy of gelatinization
$\Delta S°$	-	Entropy change of adsorption
b_T	-	Heat of adsorption (J mol^{-1})
C_e	-	Equilibrium concentration (mg L^{-1})
C_o	-	Initial Concentration (mg L^{-1})
H^+	-	Hydrogen ion
k_1	-	Rate constant of pseudso-first order model (min^{-1})
k_2	-	Rate constant of pseudso-second order model (g mg^{-1} min^{-1})
K_D	-	The distribution coefficient (L g^{-1})
K_F	-	Equilibrium adsorption constant for Freundlich model (L g^{-1})
k_i	-	Rate constant of intra-particle diffusion (mg g^{-1} $min^{-1/2}$)
K_L	-	Equilibrium adsorption constant for Langmuir model (L mg^{-1})
Ma		Moisture content
Mb	-	Bound water content
n	-	Heterogeneity factor in Freundlich isotherm
O_3	-	Ozone
q_e	-	Equilibrium adsorption capacity (mg g^{-1})
$q_{e,cal}$	-	Calculated equilibrium adsorption capacity (mg g^{-1})
$q_{e,exp}$	-	Experimental equilibrium adsorption capacity (mg g^{-1})
q_{max}	-	Maximum adsorption capacity (mg g^{-1})
q_t	-	Adsorption capacity at time t (mg g^{-1})

R	-	The gas constant (8.314 J/(mol K))
R %	-	Percentage of removal
R^2	-	Correlation coefficients
R_L	-	Separation factor in Langmuir isotherm
T	-	Absolute temperature (K)
T_c	-	End temperature
T_o	-	Onset temperature
T_P	-	Peak temperature of gelatinization
α_T	-	Tempkin isotherm constant (L g^{-1})
λ	-	Wavelength
χ^2	-	Chi-square test

LIST OF ABBREVIATIONS

BOD	-	Biochemical Oxygen Demand
$Ca(OH)_2$	-	Calcium Hydroxide
CSS-EPCH	-	Crosslinked Sago Starch with Epichlorohydrin
CSS-STMP	-	Crosslinked Sago Starch with Sodium Trimetaphosphate
DSC	-	Differential Scanning Calorimeter
EPCH	-	Epichlorohydrin
EtOH	-	Ethanol
FTIR	-	Fourier Transform Infrared
HCl	-	Hydrochloric Acid
KOH	-	Potassium Hydroxide
MB	-	Methylene Blue
Na_2CO_3	-	Sodium Carbonate
NaCl	-	Sodium Chloride
NaOH	-	Sodium Hydroxide
NH_4OH	-	Ammonium Hydroxide
$POCl_3$	-	Phosphorus Oxychloride
SEM	-	Scanning Electron Microscopy
STMP	-	Sodium Trimetaphosphate
STPP	-	Sodium Tripolyphosphate
TGA	-	Thermogravimetric Analysis
TSS	-	Total Suspended Solid
XRD	-	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Research Background

Water contamination resulting from dyes which are partly discharged into the rivers and lakes, altering the biological stability of surrounding ecosystems has aroused concern (Deng *et al*., 2011). Safe and clean water is important to reduce the chances of getting undesired effects caused by polluted water. Dyes are the main constituent used in a major process for industries such as textile, paint, tannery, paper and pulp, and dyeing in return produced a substantial amount of coloured wastewater. In addition to being aesthetically displeasing, dyes contain in water are also harmful to human health and inhibit the sunlight penetration into the water which directly destruct the aquatic ecosystem. In addition, the coloured effluence also triggers an increasing toxicity and carcinogenic harm (Wang *et al*., 2014). Therefore, these coloured wastewater effluents must to be treated before discharge.

Currently, there are many methods for the removal of dyes from industrial effluent for example flocculation (Szyguła *et al*., 2009; Verma *et al*., 2012), adsorption (Guo *et al*., 2013), filtration (Zhang *et al*., 2013; Ellouze *et al*., 2012), and biological process. Conventional technologies for waste water treatment such as oxidation, biodegradation and ozonation are not practically used to remove dyes since dyes is a stable constituent with a complex aromatic molecular structure, making it difficult to be removed (Wang *et al*., 2014). Among these technologies available, adsorption is a promising technique being practised today basically due to its being economical, simplicity of design and operation yet effective. The adsorption mechanism is referred to the gradual transition of the dye from the solution onto the surface of the adsorbent reaches a point after which allocation of the dye between the adsorbent in the solution remains unchanged.

Numerous approaches on different adsorbents such as activated carbon, saw dust, zeolites, chitin, chitosan, silica and others have been examined on the potential of dye concentrations removal from aqueous solutions. In order to enhance the adsorption capability, it becomes a major target to evolve more effective and low-cost adsorbent with a great performance of adsorption capacities. Suitable adsorbents used in dye adsorption process are activated carbon, silica, rice husk, coconut husk, saw dust, chitin, chitosan, starch and so forth. Many adsorbents have been tested for their removal ability but most of them are non-regenerable throwaway products. However, this research will assess the potential of using crosslinked sago starch as adsorbent that can be easily regenerated to absorb dye.

Next to cellulose, starch is found to be the most plentiful carbohydrate that exists from plant kingdom as a natural raw material. Sago starch is derived from Metroxylonsagu and grows well in Southeast Asian countries as a tropical crop (Abdorreza *et al*., 2012). Sago starch is qualified for the material in this research due to comparatively low-cost and abundance in Malaysia particularly in Sarawak. Being a biodegradable polymer along with well-defined chemical properties and structure, sago starch owns a great possibility as a flexible resource for numerous material applications particularly in industrial areas. Further, other characteristics possessed by sago starch include its abundance, biocompatibility, non-toxicity, and antibacterial property make it an exceptional choice for the raw material (Renault *et al*., 2008).

Hydrophilic nature in starch becomes a major constraint which can limit its application in engineering field as well as the development of starch-based material. Therefore chemical modification is applied to enhance the structure and properties of starch which become the solution for this problem where a water resistance adsorbent is then developed (Renault *et al*., 2008). Chemical modification made is expected to accumulate chemical bonds at random sites inside the granule. Hence, resulting in the stabilization of the granules as well as intensifying the relatively tender starch (Singh and Nath, 2012). Crosslinked starch slurry is highly viscous and is less prone to rupture with either extended period of heating, increasing acidic content or even harsh shaking. Cross-linking agents can provide a cross-linked sago starch to be use for various food and non-food applications. In spite of the changes in physical properties of starch by modification made through cross-linking, thermal transition characteristics can be altered as well (Mirmoghtadaie *et al*., 2009).

The sago bio-sorbent prepared in this research is expected to have a high adsorption capacity and that the desorbed sago adsorbent is recycled to adsorb the dye again and will acquire an identical adsorption capacity performance as that before the recycle. The sorbent is also expected to be technically feasible to remove dyestuffs from an aqueous solution that will reduce water pollution.

1.2 Problem Statement

The adsorption technique is a promising method amongst all techniques available in dye removal treatment due to its high efficiency, low-cost, and simplicity in design and operation (Yu *et al*., 2012). A good selection of solid sorbent becomes one of the biggest problems in adsorption technique. An adsorbent should possess characteristics of adsorbing maximum pollutant economically, biodegradable, high stability, renewable and the sources are abundant in nature. These factors have encouraged many researchers to investigate the alternative efficient and low-cost adsorbents. In this study, starch is selected since it is low-cost and renewable materials (Janaki *et al*., 2012), abundant in nature, great capability to adsorb and effective adsorbent for handling dyes (Xu *et al*., 2006). Among all starch derivatives presented, sago starch is chosen as adsorbent to remove dye since it is possess a capability to adsorb, renewable, abundant and cheaper in Malaysia.

In spite of several advantages present, sago starch suffers from its hydrophilic nature which becomes a limiting factor for developing of starch-based material. Chemical modification through crosslinking is introduced to stabilize the tender structure of sago starch. Crosslinking is the most commonly used way to modify starch, intended to add intra- or inter- molecular bond at random location of starch molecule (Gao *et al*., 2014). In this research, a crosslinked sago starch is believed to have a maximum adsorption capacity with a high potential to be easily regenerated to readsorb dye in order to reduce process cost as well as reduce the environmental problem and becomes a biodegradable dye adsorbent.

1.3 Research Objectives

Chemical modification is made to the sago starch in order to enhance the mechanical strength of adsorbent, which finally forms a crosslinked sago starch. These promising adsorbents will posses a huge potential to remove dyestuff from water through adsorption.

This study embarks on the following objectives:

i To synthesize and analyse the characterizations of crosslinked sago starch as adsorbent

ii To investigate the equilibrium isotherms, kinetics and thermodynamic study of adsoption behaviour of crosslinked sago starch in aqueous solution with respect to temperature, solution pH value, adsorbent dosage, initial concentration, contact time and temperature.

iii To assess the reusability of desorbed crosslinked sago beads to readsorb dye efficiently and examine the potential of crosslinked sago starch as an adsorbent.

1.4 Scopes of Research

The following are the scopes in this research to support the above mentioned objectives:

i) To synthesize and analyse the characterizations of crosslinked sago starch adsorbent.

Sago starch adsorbent is prepared and synthesize through a chemical modification and some other procedures as explained in Chapter 3. The characteristics of the adsorbent is analysed based on surface morphology determination on scanning electron microscope (SEM), structure and chemical composition determination by x-ray diffraction (XRD), functional group determination using Fourier transform infrared (FTIR), differential scanning calorimeter (DSC) used to study the thermal behaviour of starch including gelatanization, and finally thermogravimetric analysis (TGA) is employed to identify the stability of starch and its retrogradation properties are evaluated.

ii) To investigate the equilibrium isotherms, kinetics and thermodynamic study of adsorption behaviour of crosslinked sago starch in aqueous solution with respect to solution pH value, adsorbent dosage, initial concentration, contact time and temperature.

Batch adsorption experiments will be carried to optimize the adsorption of dye using the crosslinked sago starch at different operating conditions. In this study the ranges used for the pH are 3 to 10, adsorbent dosage is between 0.02 to 0.2 g, initial concentration is analysed at a range of 2 to 50 ppm, contact time is between 1 to 240 minutes and temperature is investigated in the range between 30 to 60^{o}C based on the previous work and screening process on adsorption capacity performance. The adsorption isotherm is necessary to describe how the interaction between the adsorbate and the adsorbent as well as provide a better understanding about adsorption capacity. In this study, the Langmuir, Freundlich and Tempkin isotherm models are employed to investigate the adsorption isotherm. The adsorption isotherms obtained were used to calculate the thermodynamic parameter.

Further, adsorption kinetics in terms of the order of the rate constant can be used to examine the dynamics of the adsorption. To analyse the experimental data obtained, three different models were applied in order to evaluate the kinetic parameters for the adsorption process which are pseudo-first-order model, pseudo-second order model and intra-particle diffusion based on the effect of adsorption time. A thermodynamic study, with respect of temperature effect where the enthalpy, entropy and Gibbs energy that show the spontaneity, is carried out.

iii) To assess the reusability of desorbed crosslinked sago starch to readsorb dye efficiently and examine the potential of crosslinked sago starch as an adsorbent.

A desorption process become an essential to be studied for the regeneration of the adsorbent and also the recovery the adsorbed compounds. Besides that, desorption studies also help to describe in details about the adsorption mechanism that occurs. After the desorption study, the performance efficiency of readsorbtion of dye was analysed. Sago starch adsorbent was then analysed to examine its potential as one of the low-cost adsorbents.

1.5 Significance of the study

A strong persistent colour and high BOD loading by substantial amount of dye wastewater effluent have led to a critical eco-system problem (Cheng *et al.*, 2009). Therefore, the treatment of dyeing effluents becomes the main concern in recent years by many researchers, and various technologies have been approached for removal of dye from the wastewater. The adsorption technique has been favoured and selected because of it is straightforward and possesses great ability, and finally the feasibility of many types of adsorbents. Choosing a capable adsorbent through adsorption procedure will enhance and provide a good quality treated effluents. Based on the need of effective and capable sorbent to remove coloured wastewater effluent, this proposal has been carried out. Dyes are extensively applied in the textile, food, paper, and pharmaceutical cosmetic industries. It is reported that over 7×10^5 metric tons of synthetic dyes are produced annually for industrial application where 5–10% from the amount is directly discharged into the environment along with the wastewater (Janaki *et al*., 2012).

This research also proposed starch, which is abundant, biodegradable and inexpensive, a natural renewable resource which is extensively used in various areas as a result from a number of good features of its own. Sago starch has attracted much attention to be used as an adsorbent in this research since it is abundant in Malaysia and possesses several other advantages. Poor adsorbing functional groups features present in native starch has caused a restricted capability of dye adsorption (Janaki *et al*., 2012). Further, in engineering the application of starch is restricted because of the weak physical properties such as mechanical strength, dimensional stability and so forth. To improve it, crosslinking reaction is applied to acquire insoluble, high surface and stable modified starch (Cheng *et al*., 2009). Several approaches have been made to alter the starch as a potential adsorbent for dyes. However, lesser application in a large scale by modified starch is due to high cost is needed and is not feasible. Therefore, starch based adsorbent is synthesized for the removal of dye from aqueous solution. Thus, in order to achieve an economical and environmental friendly sorbent, crosslinked sago starch will be used in this study.

As a result, it will also keep the environment safe because the used adsorbent will be regenerated and desorb the adsorbed dye to be reabsorbed back as much pollutant as they can. The optimum parameter for crosslinked sago starch will be determined through this research. The cost of sago starch itself was assumed low and only needed to purchase crosslinking agents in order to enhance the adsorption process. There is no abandoned secondary waste will be produced. Therefore, this research is economic and has an ecological approach. This research can be a reference for commercial and industrial production and application. This study is expected to be a solver to the problem to get the effective sorbent of coloured wastewater nowadays.

1.6 Thesis Outline

The thesis is presented into five main chapters and each chapter explains the sequence of this research. Chapter 1 presents brief overview about the general information and introduction to this research along with the problem statement, research objectives, scopes of research, significance of study, thesis outline and summary of this chapter. Chapter 2 explains the deep view of related knowledge about dye pollutant and the available treatment methods nowadays, the reason why adsorption is the preferable method, the advantages and flaws of available treatment is also reviewed. Moreover, sago starch as a chosen material and its wide application in industrial area also will be discussed. Chapter 3 covers the research methodology where experimental procedures including synthesis of adsorbent, characterizations of adsorbent, adsorption process, and degeneration will be deliberated. Chapter 4 will briefly explain on the result and discussion of this research. Meanwhile, Chapter 5 presents the conclusion of this research and future work recommendations.

1.7 Summary

The research background, problem statements, research objectives, scopes of research, the significance of the study and finally the thesis outline are thoroughly presented and explained in this chapter. Generally, this research is conducted in order to remove dye stuff from aqueous solution and which will be implemented in the real solution. Dye as a hazardous contaminant in water which leads to unpleasant effect even if its existence is in a small amount. Thus, the removal of dye will eventually help to curb water contamination where low-cost adsorbent yet effective is employed rather than using the expensive ones. Two solutions will be directly covered in one research which is the water pollution caused by dye contamination as well as the cost reduction in this adsorption process.

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